New Analytical Modalities for Soil Carbon Analysis: The Inelastic Neutron Scattering System

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Abstract

Cardinal to improving our understanding of the belowground carbon processes and transport and to determining terrestrial carbon stocks is to improve the instrumentation for analyzing soil carbon. The belowground processes, hidden to human eyes, are assessed directly at present, by taking samples from the field to the laboratory, and indirectly, by eddy covariance towers measuring CO_2 fluxes. The scope of these basic approaches is limited, and they are inadequate for present and future needs for quantitative determinations of transient- and steady-state C levels in soil. A new generation of analytical modalities is emerging that measure soil carbon *in situ:* they are non-destructive, inexpensive, and can scan large fields. We give an overview of a one newly emerging modality, an inelastic neuron scattering system.

Key Words: Soil analysis, inelastic neutron scattering, fast neutrons, gamma-ray spectroscopy, carbon sequestration.

Introduction

The unabated rise in atmospheric CO_2 and the consequential changes in climate have strengthened the resolve of the Office of Science (SC), U.S. Department of Energy (DOE), to improve understanding of terrestrial carbon processes (TCP) that would assist in predicting carbon cycles and their relation to climate change. One of the several goals of the TCP programs specifically is that of quantifying terrestrial carbon sources and sinks which, in turn, requires an understanding of the underground processes and dynamics that ultimately determine its fate. Similar considerations and needs recently were echoed in the Subcommittee of the Biological and Environmental Research Advisory Committee's report stating the need for developing an integrated database of carbon turnover times in the soil across climate and bioregions, thereby providing constraints for terrestrial carbon models [BERAC, 2005]. The report notes that despite notable progress toward detailing carbon turnover at local levels, existing programs and models are inadequate in particularizing the fate of carbon across North America. Fundamental in these knowledge gaps is the lack of the comprehensive databases required for the accuracy of the models, which stems from the difficulties in sampling the soil for carbon analysis, and the requirement to cover large areas in national- and global-scale modeling. Such databases are important since carbon turnover varies in different climates, environments, and soil types [Scharpenseel and Pfeiffer, 1998; Greenland, 1998]. Moreover, the models themselves need verification once the predictions are made. Models are only approximate representations of reality to the best of our understanding; thus, it pays to bear in mind the phrase "all models are wrong; some are useful" with all its ramifications [Jones et al. 2005]. The criticality of having a better understanding of the belowground processes and carbon sequestration is not restricted to research on carbon cycles; these processes play pivotal roles in the long-term quality (productivity) of the soil, while also reducing atmospheric CO_2 pollution. Furthermore, implementing trading in carbon credits strongly depends on the availability of dependable instrumentation for monitoring and verifying the stocks of sequestered carbon in the field.

Soil is a complex three-phase matrix convoluted with organic and inorganic matter containing living and dead organisms, aggregated into an underground system whose activities are concealed. When the "black box" of this soil mélange is dissected for study, its function is altered [Johnston et al., 2004]. This fact, compounded by the physical variability in the soil's composition, the presence of stones, debris, and litter is only part of the complexities inherent in measuring the soil's parameters. Hence, it is unlikely that any single system will attend to all the issues. Below surface processes presently are assessed both directly, by taking samples from the field into a laboratory for chemical analysis, and, indirectly, by eddy covariance towers measuring differences in CO_2 fluxes to estimate net terrestrial gains or loses in carbon. Lal et al. [2001] discuss the many considerations, issues, and errors associated with gathering soil samples and preparing them for Carbon-Hydrogen-Nitrogen (CHN) dry-combustion chemical analysis. Eddy covariance methodology, its characteristics and limitations, are well described on the AmeriFlux web site [Ameriflux]. These two basic current approaches established a few decades ago represent time- and space- averaged point measurements that are being extrapolated to regional-, national-, and global-scales. It is hard to envision how current sampling practices for the CHN analysis of soil can suddenly be improved and significantly expanded to cover the new large areas required for strengthening our databases, nor, for that matter, how it can be achieved by increasing adequately the number of AmeriFlux towers. Even with marginal improvements over time, the scope of these methods will remain too narrow, while their accuracy and repeatability is becoming more and more inadequate for present-day and future needs to quantitatively determine transient- and steady-state carbon levels in soil. These shortcomings were identified in the executive summary of a DOE report on Carbon Sequestration Research and Development, which stated that one R&D need is to "Improve measurement of gross carbon fluxes and dynamic carbon inventories through improvements to existing methods and through development of new instrumentation for *in situ*, non-destructive belowground observation and remote sensing to allow aboveground biomass measurement, verification, and monitoring of carbon stocks" [DOE/OS Report, 1999]. Similarly, in the Proceedings of the St. Michaels Workshop, Post et. al. [1999] showed a table indicating a mid-term (2002-2007) need for "Non-destructive field measurement (exp.)"; this ability did not materialize until recently. In short, current analytical methodologies are not on par with the needs for a fast, reliable, *in situ,* non-destructive, static/dynamic, and inexpensive instrumentation.

Nevertheless, sporadic publications and conference presentations herald the appearance of new analytical modalities for carbon analysis in soil that are superior to the well- entrenched and unchanging traditional methods. They are based on sound physical principles, and offer *in situ* atomic- and chemical-speciation of carbon distribution in soil that was not previously possible. The proclaimed virtues of each method culminated in a recent dedicated workshop, the first of its kind, on "Emerging Modalities for Soil Carbon Analysis: Sampling Statistics and Economics Workshop" held at BNL [BNL, 2006] during which it become abundantly clear that all of them had reached a degree of maturity where they need to be brought side-by-side for complete characterization and evaluation of their usefulness.

Table 1 summarizes the fundamental characteristics of the newly emerging carbon analysis modalities. Additional information is given for LIBS in [Ebinger et al., 2003; Cremers et al., 2001], for NIR in [Chang et al., 2001; Ehsani et al., 1999; Fystro, 2002; Reeves et al., 1999; Shepherd et al., 2002; and Viscerra Rossel et al., 2005], and for Py-MBMS in [Evans et al. 1984,

1987, Winding et al., 1987, and Agblevor et al., 1994]. Here, we provide more details on the Inelastic Scattering System (INS) that is completely non-destructive in *in situ* measurements, can be operated in a static or a scanning modes, and, during the analysis covers an approximate volume of about 0.3 m^3 to a depth of about 25 cm.

Table 1 Basic Characteristics of the Emerging Modalities for Soil Carbon Analysis.						
Instrument	Process	Methodology	Radiation Type Detected	Penetration Depth (cm)	Sampled Volume (cm^3)	Measurement Type
LIBS	Atomic	Plasma Induced Emission	Visible	~ 0.1	10^{-2}	Point, Depth Profile, Destructive
NIR	Molecular	Diffuse Reflectance	Near-Infrared	~ 0.2	10^0	Surface, Scanning, Destructive
MIR	Molecular	Diffuse Reflectance	Infrared	~ 1	10^1	Surface, Destructive
P-MBMS	Molecular	Pyrolysis Molecular Beam	m/z	---	10^1	Samples Destructive
INS	Nuclear	Neutron Induced Nuclear Reactions	Gamma Rays	~ 30	10^5	Volume, Scanning, Non-Destructive

INS System

INS is a nuclear method based on fast 14 MeV neutrons interacting with nuclei of the soil's elements via inelastic-, elastic-, and capture-reactions, thereby inducing the emission of characteristic gamma rays. Consequently, INS measurements are unaffected by the chemistry of the elements being analyzed. In addition, these processes occur very fast, in a time scale of microseconds, thus facilitating stationary and scanning measurements. A mobile system consisting of a neutron generator (NG), shielding, NaI detectors and nuclear electronics is shown in Fig. 1. An array of NaI detectors, mounted
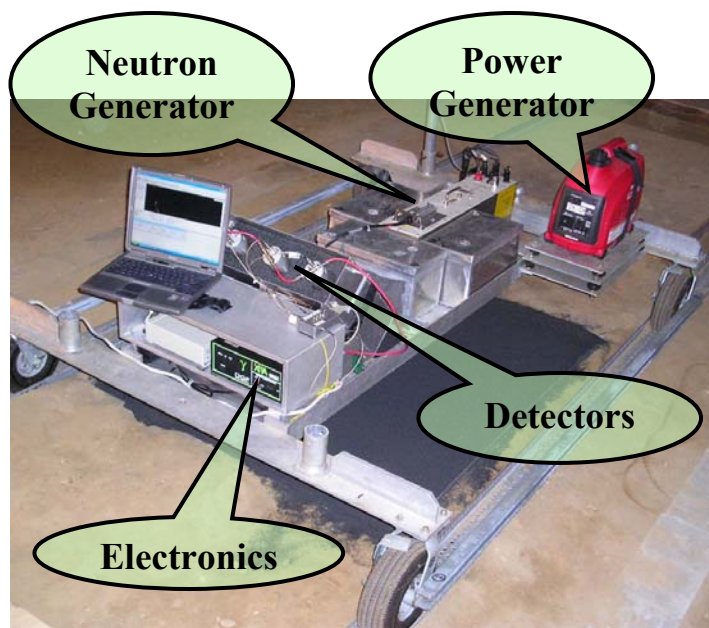

Figure 1 Alpha prototype of the mobile INS system.

beside a neutron generator, provides for multi-elemental quantitative gamma-ray spectroscopy [Wielopolski et al., 2003, Wielopolski et al., 2005].

The system was calibrated using synthetic soils consisting of a homogeneous mixture of sand with known amounts of carbon, and subsequently was used in three field studies in static and scanning modes. Alternatively, since the response function of the INS system is known, the calibration can be derived analytically from basic principles using fundamental parameters. The INS system, mounted on a cart, hovers about 30 cm above the ground, is totally non-destructive, and can be towed over large areas by a small MPV. In a static mode, the sampled volume (V_0) by the INS system is about 0.3 meter cube to an approximate depth of 25 cm. However, in a continuous scanning mode the volume seen by the system is increased from V_0 to V_0 plus A_c times vt, where v is the scanning speed, t is the scanning time, and A_c is the depth cross-section of the sampled volume. Thus, in a static measurement, the time it resides over a given point is traded for larger volume seen by the scanning system; for a homogeneous soil. This trade-off is summarized in Table 2. In Fig. 3 we show the volumes engulfing 90%, 95%, and the 99% of the total signal during static measurements, from which the cross section A_c might

Carbon Calibration in a Sandpit

$y=73100(\pm4040)Cc+5295(\pm23)$

$y_{corr}=67846(\pm4112)Cc - 339(\pm333)$

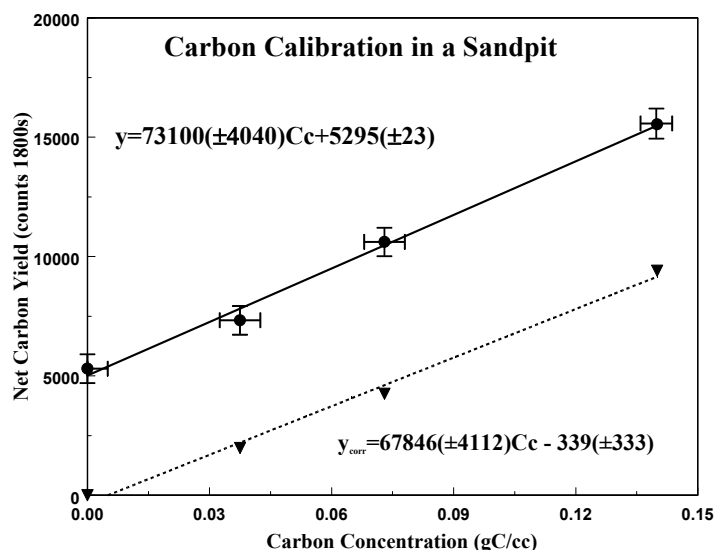*(x-axis: Carbon Concentration (gC/cc); y-axis: Net Carbon Yield (counts 1800s))*

Figure 2 System calibration using synthetic soil mixtures of sand with granular carbon. Upper line net counts in the carbon peak, bottom line corrected for Si interferences.

be surmised as being bell shaped. Table 3 summarizes the footprints, volumes, and the sampled depth. We note that some variations in the values reported in it are expected with changes in the soil's bulk density or moisture content. The scanned area will be measured with a GPS (global positioning system) mounted on the cart.

For a given sensitivity of the system, the signal S, in units of counts/gC, is proportional to the counting time, whereas the error is proportional to the square root of the counting; thus, increasing the counting time improves the signal-to-noise ratio and the minimum detectable limit for carbon. Since during

Table 2 Comparison of net carbon yield from static measurements versus dynamic scans both counted for 1800 s			
	Mean Static Counts	**Dynamic Counts**	**Difference In SD**
Hiwassee Clay (V_1)	19,229	19,091	$0.1\sigma_{n-1}$
Vaiden Silty Clay ($2V_1$)	26,783	25,564	$0.8\sigma_{n-1}$
Hiwassee Sandy Loam (Random V)	30,449	31,117	$0.7\sigma_{n-1}$

scanning the counting time is traded for the larger sample volume seen by the system, the effect on the error is similar. For a constant scanning speed, the INS response represents the true mean value for the entire field.

Figure 3 Surfaces describing the volumes from which a 90, 95 and 99% of the carbon gamma rays signal intercepts the detectors.
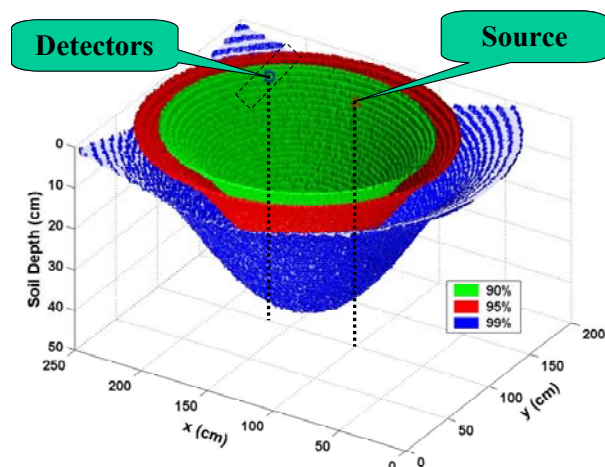
Table 3 Depth, footprint, and volume engulfed by the described volumes.

% of Total Response	Depth (cm)	Footprint (m^2)	Volume (m^3)	Mass (kg)
90	25	2.400	0.233	325.66
95	31	3.345	0.373	522.18
99	44	7.069	0.789	1105.29

Summary

We have presented the basic parameters and characteristics of the INS system. The system is amenable for static- and dynamic-measurements in the field, and has the advantage of being completely nondestructive, thus enabling sequential measurements at the same spot and over the same area. The error propagation in measuring large fields is also reduced since a single measurement represents the mean value of carbon for the entire field. Whilst we have shown that the net carbon yield from a scanning system is similar to that from a stationary system, the value of systematically incorporating INS measurements into a database for modeling remains to be verified.

Acknowledgement

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